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(54) Title: METHOD OF USING CATIONIC CHARGE MODIFIED FILTER

(57) Abstract

A method of removing a substantial portion of waterborne pathogens from an aqueous liquid contaminated with such waterborne pathogens. The method includes the steps of passing the contaminated aqueous liquid through a chemically charge-modified filter composed of: 1) a filter sheet having a plurality of individual exposed cellulose fibers and silica based filter materials selected from silica particulates and siliceous fibers; and 2) cationic chemical charge modifiers coated on surfaces of the filter sheet. When the contaminated aqueous liquid is passed through the chemically charge-modified filter, a substantial portion of the waterborne pathogens greater than about 0.1 micron in size are adsorbed onto the chemically charge-modified filter. The filter is effective at removing *Vibrio cholerae*.

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METHOD OF USING CATIONIC CHARGE MODIFIED FILTER

FIELD OF THE INVENTION

This invention relates to a method of filtering aqueous liquids.

BACKGROUND OF THE INVENTION

Apertured films, woven fabrics and nonwoven materials have been used as filter sheets for removing or separating particles from liquids. Generally speaking, methods of filtering liquids that utilize such filter sheets rely on some form of mechanical straining or physical entrapment that can present limitations when the size of the particle to be removed is very small, especially particles of less than one micron in diameter.

Improved filters have been developed with modified surface charge characteristics to capture and adsorb particles by electrokinetic interaction between the filter surface and particles contained in an aqueous liquid. Some filters have been used in processes reported to be effective in removing specific virus particles and pyrogens. The reported literature appears to describe use of such charge-modified filter materials only for capturing and concentrating waterborne enteric viruses for sampling large water sources (e.g., lakes, rivers, effluent).

One phenomena observed with some filters having modified surface charge characteristics is that the filters have different filtration efficiencies for different types of particles and/or organisms, such as, for example, different types of virus. That is, some filters having modified surface charges provide acceptable removal of some types of organisms (e.g., some types of virus) but not others. The nature of this affinity appears to be difficult to predict. In some cases, the affinity exists under only carefully controlled circumstances.

Since even relatively small differences in removal efficiency can be very important if the organism being removed is pathogenic, the discovery that a filter or filter system has an unpredictably strong affinity for a pathogenic organism would be both unexpected and highly desirable, especially if the filter can be used to produce potable water.

Thus, there is a need for a simple, practical and inexpensive method for removing pathogenic organisms from aqueous liquid. This need also extends to a simple method for removing pathogenic organisms from aqueous liquid utilizing a practical and inexpensive chemically charge-modified filter. Meeting this need is important because removing pathogenic organisms from aqueous liquids in a practical and inexpensive manner remains a challenge in many parts of the world.

DEFINITIONS

As used herein, the term "chemical charge modifier" refers to polymeric material capable of coating a substrate and providing a cationic charge site. Chemical charge modifiers may be cationic polymers such as, for example, quaternary amine containing cationic resins, aliphatic polyamines having at least one primary amine or at least two secondary amines, and the like. It is contemplated that chemical charge modifiers may be cationic polymer systems composed of a primary polymer material and a secondary polymer material. For example, the cationic polymer system may be composed of a primary polymer material such as polyamine epichlorohydrin and a secondary polymer material such as tetraethylene pentamine. Exemplary chemical charge modifiers may have a positive charge and, when present in a liquid having a dielectric constant sufficient for separate charged particles to exist, can be incorporated, coated or adsorbed onto a substrate to modify the coating so that cationic species and/or positively charged particles are present at the surface of the coating under the appropriate conditions.

As used herein, the term "chemically charge-modified" refers to the incorporation of chemical charge modifiers (e.g., cationic polymers) onto a substrate. Generally speaking, charge modification occurs when the chemical charge coated substrate is in contact with aqueous liquid under appropriate conditions so that cationic species and/or positively charged particles are present on the surface of the coating.

As used herein, the term "waterborne pathogens" refers to microorganisms existing in water or aqueous liquids that are capable of causing disease. For purposes of the present invention, waterborne pathogens are microorganisms greater than 0.1 micron in size and excludes the class of pathogens commonly referred to as "viruses." Exemplary waterborne pathogens include, but are not limited to, *Vibrio cholerae*, *Eshcerichia coli*, *Salmonella typhimurium*, *Shigella flexineri*, *Campylobacter jejuni*, *Pseudomonas aeruginosa*, *Giardia lamblia*, *Cryptosporidium parvum*, and *Staphylococcus aureus*.

As used herein, the term "adsorbed" refers to a type of adhesion which takes place at the surface of a solid in contact with another medium (e.g., a liquid), resulting in the accumulation or increased concentration of molecules from that medium in the immediate vicinity of the surface.

As used herein, the term "nonwoven web" refers to a web that has a structure of individual fibers or filaments which are interlaid, but not in an identifiable repeating manner. Nonwoven webs have been, in the past, formed by a variety of processes known to those skilled in the art such as, for example, m ltblowing, spunbonding, wet-forming and various bonded carded web processes.

As used h rein, the term "she t" refers to a mat rial that can be a woven fabric, knit fabric, nonwoven fabric or film-lik material (e.g., an apertured film-like material).

As used herein, the term "consisting essentially f" does not exclude the presence of additional materials which do not significantly affect the desired characteristics of a given composition or product. Exemplary materials of this sort would include, without limitation, pigments, antioxidants, stabilizers, surfactants, waxes, flow promoters, particulates or materials added to enhance processability of a composition.

SUMMARY OF THE INVENTION

The problems described above are addressed by the present invention which is directed to a method of removing a substantial portion of waterborne pathogens from an aqueous liquid contaminated with such waterborne pathogens. The method includes the steps of passing the contaminated aqueous liquid through a chemically charge-modified filter composed of: 1) a filter sheet having a plurality of individual exposed cellulose fibers and silica based filter materials selected from silica particulates and siliceous fibers; and 2) cationic chemical charge modifiers coated on or bonded to surfaces of the filter sheet.

The chemical charge modifiers include: 1) a primary charge modifier composed of a water soluble organic polymer capable of being adsorbed onto the filter sheet and having a molecular weight of greater than about 1000, each monomer of the polymer having at least one epoxide group capable of bonding to the individual exposed surfaces of the filter sheet and also having at least one quaternary ammonium group; and 2) a secondary charge modifier bonded to a portion of the epoxy groups on the organic polymer, wherein the secondary charge modifying agent is an aliphatic polyamine having at least one primary amine or at least two secondary amines. According to the method of the invention, when the contaminated aqueous liquid is passed through the chemically charge-modified filter, a substantial portion of the waterborne pathogens greater than about 0.1 micron in size are adsorbed onto the chemically charge-modified filter.

In the method of the present invention, the waterborne pathogens may be greater than about 0.1 micron in size. According to an aspect of the invention, the waterborne pathogens may be selected from *Vibrio cholerae*, *E. coli*, *S. typhimurium*, *S. flexineri*, *C. jejuni*, *P. aeruginosa*, *G. lamblia*, *C. parvum* and *S. aureus*.

In another aspect of the invention, the reduction of *Vibrio cholerae* is desirably greater than a log 3 reduction. For example, the reduction of *Vibrio cholerae* is desirably greater than a log 5 reduction. Acceptable reductions of *Vibrio cholerae* may be achi ved und r a variety of conditions. For xample, satisfactory reductions of *Vibrio cholerae* may be achieved when

the waterborne pathogen contaminated aqueous liquid has a pH ranging from about 5 to about 9.

According to the invention, the chemical charge modifiers may be cationic polymers such as, for example, quaternary amine containing cationic resins, aliphatic polyamines having at least one primary amine or at least two secondary amines, and the like. In one aspect of the invention, the chemical charge modifiers may be cationic polymer systems composed of a primary polymer material and a secondary polymer material. For example, the cationic polymer system may be composed of a primary polymer material such as polyamine epichlorohydrin and a secondary polymer material such as tetraethylene pentamine.

The filter sheet is desirably composed of cellulose fiber and silica based filter materials selected from silica particulates and siliceous fibers (e.g., glass fibers).

It is contemplated that the filter sheet may contain cellulose fiber in combination with some other fibrous or particulate material. Exemplary fibrous materials include meltblown fibers, spunbond filaments and/or various staple fibers.

According to the method of the present invention, the chemically charge-modified filter may have a basis weight of from about 6 to about 400 grams per square meter (gsm). For example, the chemically charge-modified filter may have a basis weight of from about 12 to about 250 grams per square meter. As a further example, the chemically charge-modified sheet may have a basis weight of from about 17 to about 102 grams per square meter.

The present invention encompasses a method of removing waterborne pathogens from aqueous liquid utilizing a multi-layer filter material including at least two layers of the chemically charge-modified filter described above. The present invention also encompasses a method utilizing a multi-layer material including at least one layer of the chemically charge-modified filter described above and at least one other layer. The other layer may be selected from woven fabrics, knit fabrics, bonded carded webs, continuous spunbond filament webs, meltblown fiber webs, films, apertured films, and combinations thereof.

The present invention also encompasses a method of removing waterborne pathogens from aqueous liquid utilizing the chemically charge-modified filter described above in a three-dimensional form or shape such as, for example, a tube, cylinder, cone, cube, sphere or the like.

The method of the present invention described above further encompasses a method of removing a substantial portion of waterborne pathogens greater than 0.1 micron in size from water contaminated with such waterborne pathogens to produce potable water. The method includes the step of passing the contaminated water through the chemically charge-

modified filter described above so that a substantial portion of the waterborne pathogens greater than 0.1 micron in size is adsorbed onto the chemically charge-modified filter.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a micrograph of an exemplary chemically charge-modified filter material.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a method of removing a substantial portion of waterborne pathogens from an aqueous liquid contaminated with such waterborne pathogens. The method includes the steps of passing the contaminated aqueous liquid through a chemically charge-modified filter composed of: 1) a filter sheet having a plurality of individual exposed cellulose fibers and silica based filter materials selected from silica particulates and siliceous fibers; and 2) cationic chemical charge modifiers coated on surfaces of the filter sheet.

The filter sheet is desirably composed of cellulose fiber and silica based filter materials selected from silica particulates and siliceous fibers (e.g., glass fibers). The cellulose fibers may be wood pulp having a diameter ranging from about 6 to about 60 microns and lengths ranging from about 0.85 to about 6.5 millimeters. It is desirable to have greater than about 50%, by weight, of the filter sheet be particulate materials.

Suitable siliceous particulates include, for example, clays, talc, diatomaceous earth or the like. Siliceous fibers (e.g., glass fibers) may be used alone or may be mixed with the siliceous particulates.

It is contemplated that the filter sheet may contain cellulose fiber in combination with some other fibrous or particulate material. Exemplary fibrous materials include meltblown fibers, spunbond filaments and/or various natural and/or synthetic fibers.

If the fibrous materials are meltblown fibers, they may include meltblown microfibers. The fibrous materials may be formed from thermoplastic polymers or thermoset polymers. If the fibrous materials are formed from a polyolefin, the polyolefin may be polyethylene, polypropylene, polybutene, ethylene copolymers, propylene copolymers and butene copolymers. The fibers and/or filaments may be formed from blends that contain various pigments, additives, strengthening agents, flow modifiers and the like. Such fabrics are described in U.S. Patent Nos. 4,041,203, 4,374,888, and 4,753,843, the contents of which are incorporated herein by reference. Those patents are assigned to the Kimberly-Clark Corporation, the assignee of the present invention.

In some embodiments of the invention, it is contemplated that the filter sheet may be formed by adding fibers and/or particulates to the gas stream in which meltblown fibers are carried so that an intimate entangled commingling of meltblown fibers and other materials, e.g., wood pulp, staple fibers and particulates such as, for example, activated carbon, silica particulates, clays, or the like, occurs prior to collection of the meltblown fibers upon a collecting device to form a coherent web of randomly dispersed meltblown fibers and other materials such as disclosed in U.S. Patent Nos. 4,100,324, and 5,350,624, the disclosure of which is hereby incorporated by reference.

It is also contemplated that the fibrous material in the filter sheet may be joined by interfiber bonding to form a coherent web structure. Interfiber bonding may be produced by entanglement between individual meltblown fibers, carded fibers, spunbond filaments and/or other fibrous materials. Some fiber entangling is inherent in the meltblown process, bonding-carding process and/or spunbond process but may be generated or increased by processes such as, for example, hydraulic entangling or needlepunching. Alternatively and/or additionally a bonding agent may be used to increase the desired bonding. If at least a portion of the fibrous material in the filter sheet is cellulosic fibrous material, some interfiber bonding may be attributable to "paper" bonding.

The filter sheet may have a basis weight ranging from about 6 gsm to about 400 gsm. For example, the filter sheet may have a basis weight ranging from about 12 gsm to about 250 gsm. As a further example, the filter sheet may have a basis weight ranging from about 17 gsm to about 102 gsm. It is contemplated that, after processing, any number of treated filter sheets may be joined together or treated filter sheets may be joined to other materials to form a consolidated material that may have a basis weight within the range of 6 gsm to 400 gsm or even greater (e.g., 400 gsm or more).

According to the invention, the chemical charge modifiers include: 1) a primary charge modifier composed of a water soluble organic polymer capable of being adsorbed onto the filter sheet and having a molecular weight of greater than about 1000, each monomer of the polymer having at least one epoxide group capable of bonding to (or coating) the individual exposed surfaces of the filter sheet and also having at least one quaternary ammonium group; and 2) a secondary charge modifier bonded to a portion of the epoxy groups on the organic polymer, wherein the secondary charge modifying agent is an aliphatic polyamine having at least one primary amine or at least two secondary amines; a filter sheet having a plurality of individual exposed surfaces.

Exemplary cationic polymers include, but are not limited to, quaternary amine containing cationic resins, aliphatic polyamines having at least one primary amine or at least

two s condary amines, and the like. In one aspect of the inv ntion, the chemical charge modifiers may be cationic polym r systems composed of a primary polymer material and a secondary polymer material. For example, th cationic polymer system may be composed of a primary polymer material such as polyamine epichlorohydrin and a secondary polymer material such as tetraethylene pentamine.

Exemplary chemically charge-modified filters composed of: 1) a filter sheet having a plurality of individual exposed cellulose fibers and silica based filter materials selected from silica particulates and siliceous fibers; and 2) cationic chemical charge modifiers coated on or bonded to surfaces of the filter sheet are described in U.S. Patent No. 5,085,784, issued Feb. 4, 1992, to Ostreicher, and U.S. Patent No. 4,981,591, issued Jan. 1, 1991, to Ostreicher. Such chemically charge-modified filters may be obtained from CUNO, Process Filtration Products, A Unit of Commercial Intertech Corporation, Meriden, Connecticut, under the trade designation Zeta Plus® VIROSORB® 1MDS.

Although these chemically charge-modified filter materials are disclosed as useful for capturing and concentrating waterborne enteric viruses for sampling large water sources (e.g., lakes, rivers, effluent), the reported literature appears to recognize only that use. The present invention relates to the discovery of the unexpected affinity of these materials for certain waterborne pathogens greater than 0.1 microns (i.e., 0.1 micrometers) in size and that these charge-modified filters may be utilized in a method to remove an unexpectedly substantial portion of such waterborne pathogens from aqueous liquid. The present invention also relates to the discovery that these charge-modified filters may be utilized in a method to remove an unexpectedly substantial portion of waterborne pathogens greater than 0.1 microns in size from aqueous liquid to produce potable water.

When the contaminated aqueous liquid is passed through the chemically charge-modified filter, a substantial portion of the waterborne pathogens greater than about 0.1 micron in size are adsorbed onto the chemically charge-modified filter. Various flow rates of aqueous liquid through the filter may be used and appropriate flow rates can readily be determined by conventional methods.

Generally speaking, the waterborne pathogens are be greater than about 0.1 micron in size. According to an aspect of the invention, the waterborne pathogens may be selected from *Vibrio cholerae*, *E. coli*, *S. typhimurium*, *S. flexineri*, *C. jejuni*, *P. aeruginosa*, *G. lamblia*, *C. parvum* and *S. aureus*. Of course, while there may be other waterborne pathogens that could be removed from aqueous liquid with unexpectedly good filtration efficiencies, the present invention has been found to be particularly effectiv at removing *Vibrio cholerae* from aqu ous liquid.

Accordingly, in an aspect of th invention, th reduction of *Vibrio cholerae* by practicing th described method is desirably greater than a log 3 reduction. For xample, th reduction of *Vibrio cholerae* is d sirably greater than a log 5 reduction. Acceptable reductions of *Vibrio cholerae* may be achieved under a variety of conditions. For example, satisfactory reductions of *Vibrio cholerae* may be achieved when the waterborne pathogen contaminated aqueous liquid has a pH ranging from about 5 to about 9.

The present invention encompasses a method of removing waterborne pathogens from aqueous liquid utilizing a multi-layer filter material including at least two layers of the chemically charge-modified filter described above. Multiple layers of the filter material may be used to provide greater total surface area and/or other effects which may increase filtration efficiency. The present invention also encompasses a method utilizing a multi-layer material including at least one layer of the chemically charge-modified filter described above and at least one other layer. The other layer may be selected from woven fabrics, knit fabrics, bonded carded webs, continuous spunbond filament webs, meltblown fiber webs, films, apertured films, and combinations thereof. It is contemplated that the other layer may be selected to function in a variety of ways. For example, a meltblown fiber web may be used to provide removal of gross contaminants from aqueous liquid. Textile or spunbond fabrics may be selected to provide reinforcing or strength to the filter. Other materials may be selected to provide bulk or strength to enhance handling of the filter or to facilitate assembly or construction of filter laminates, cartridges or the like.

The present invention also encompasses a method of removing waterborne pathogens from aqueous liquid utilizing the chemically charge-modified filter described above in a three-dimensional form or shape such as, for example, a tube, cylinder, cone, cube, sphere or the like. Generally speaking, the particular shape or configuration of the filter for an application may be determined by conventional methods.

An important aspect of the present invention described above further encompasses a method of removing a substantial portion of waterborne pathogens greater than 0.1 micron in size from water contaminated with such waterborne pathogens to produce potable water. The method includes the step of passing the contaminated water through the chemically charge-modified filter described above so that a substantial portion of the waterborne pathogens greater than 0.1 micron in size is adsorbed onto the chemically charge-modified filter.

EXAMPLES

PARTICLE ADSORPTION

Uniformity of Particle Adsorption

FIG. 1 illustrates the comparable uniformity of particle adsorption for an exemplary charge-modified glass/cellulose filter medium (Zeta Plus® VIROSORB® 1MDS, CUNO, Meriden, CT). In particular, FIG. 1 is a 1000X linear magnification photomicrograph of a filter sheet with adsorbed polystyrene particles (300-nm in diameter). An aqueous solution containing polystyrene particles at a concentration of 1.7×10^9 particles/mL was passed through the filter sheet mounted in a hand-held syringe disk filter apparatus (MILLIPORE 25mm diameter - available from Millipore Corporation, Bedford, Massachusetts). A 5 mL aliquot of particle solution was passed through the filter sheet in approximately 30 seconds, followed by air to remove any excess liquid. The filter sheet was then rinsed with a 5-20 mL volume of deionized water to remove any loosely-bound particles, which was then followed again by air to remove any excess liquid.

A sample was submitted for field emission scanning electron microscopy (SEM) analysis to determine the uniformity and amount of particle adsorption to individual fibers. SEM analysis was carried out using a Hitachi S4500 field emission scanning electron microscope. From the micrograph, it is evident that the exemplary charge-modified glass/cellulose filter exhibits generally uniform particle adsorption.

WATERBORNE PATHOGEN ADSORPTION

As discussed above, the method of the present invention utilizes certain chemically charge-modified filters to remove substantial portions of waterborne pathogens greater than about 0.1 micron in size from aqueous liquid contaminated with such waterborne pathogens. For purposes of the present invention, the expression "removing a substantial portion of waterborne pathogens greater than about 0.1 micron in size from water contaminated with such waterborne pathogens" generally refers to removal of at least about 90 percent of the waterborne pathogens. In many instances, the removal rate will be significantly greater. For example, in some cases removal rates of 99 percent (a log 2 reduction) have been achieved. Removal rates of 99.9 percent (log 3 reduction), 99.99 percent (log 4 reduction), 99.999 percent (log 5 reduction) or greater have been achieved.

The filters of the present invention remove waterborne pathogens primarily by interactions between the surface charg on the filter material and the pathogens rather than

by physical entrapment. Evidence that this is the cas may be found in a comparison of the effectiv equivalent pore siz of various filter material.

Effective Equivalent Diameter of Pores

Measurements were made of the effective equivalent diameter of pores in three different types of filter material. Pore sizes were determined by liquid displacement techniques utilizing a Coulter Porometer and Coulter POROFILÔ test liquid available from Coulter Electronics Limited, Luton, England. The mean flow pore size is determined by wetting a test sample with a liquid having a very low surface tension (i.e., Coulter POROFILÔ). Air pressure is applied to one side of the sample. Eventually, as the air pressure is increased, the capillary attraction of the fluid in the largest pores is overcome, forcing the liquid out and allowing air to pass through the sample. With further increases in the air pressure, progressively smaller and smaller holes will clear. A flow versus pressure relationship for the wet sample can be established and compared to the results for the dry sample. The mean flow pore size is measured at the point where the curve representing 50% of the dry sample flow versus pressure intersects the curve representing wet sample flow versus pressure. The diameter of the pore which opens at that particular pressure (i.e., the mean flow pore size) can be determined from the following expression:

$$\text{Pore Diameter (Microns)} = (40t)/\text{pressure}$$

where t = surface tension of the fluid expressed in units of mN/M; the pressure is the applied pressure expressed in millibars (mbar); and the very low surface tension of the liquid used to wet the sample allows one to assume that the contact angle of the liquid on the sample is about zero.

The mean flow pore diameter was measured for a Millipore 0.5 micron filter available from Millipore Corporation, Bedford, Massachusetts; a Zeta Plus® Virosorb® 1MDS media disc available from CUNO, Meriden, Connecticut; and a 0.5 osy (~17 gsm) polypropylene meltblown nonwoven fabric available from Kimberly-Clark Corporation, Roswell, Georgia. The results of pore size testing are reported in Table 1. The MILLIPORE filter and the Virosorb® filter have mean flow pore sizes of about 35 times and about 5.9 times smaller, respectively, than 0.5 osy (~17 gsm) polypropylene meltblown nonwoven. It should be noted that the pore sizes measured for the Virosorb® filter and the polypropylene meltblown are greater than the diam ters of at many types of waterborne pathogens including, for example, *Vibrio Cholerae*.

Vibrio Cholera and Bacterial Filtration

Samples f Zeta Plus® Virosorb® 1MDS media disc were tested for their ability to filter or remove *Vibrio cholera* from aqueous solution. The *Vibrio cholerae* were plated and an isolated colony was inoculated in 5 mL of sterile tryptic soy buffer which was incubated at 35 degrees Centigrade for 3 hours. The *Vibrio cholerae* solution was measured at 420 nm and diluted until the absorbance was 0.64 for an approximate titer of $1x10^8$ waterborne pathogens per mL. One mL of the *Vibrio cholerae* solution was added to one liter of sterile water for an approximate initial titer of $1x10^5$ organisms per mL.

Zeta Plus® Virosorb® 1MDS media discs having a diameter of 48 mm were placed in a filter vacuum apparatus. Two layers of filters were used to provide a total basis weight of approximately 35-40 grams per square meter. Approximately 40 mL of the cholera solution was filtered through the filters. The filtrate was serially diluted by adding 1 mL of filtrate to 9 mL of phosphate buffer solution (NaCl, Na_2HPO_4, KH_2PO_4 and distilled H_2O). Approximately 0.1 mL of each dilution (0, -1, -2, -3, -4) was plated on 1% tryptic soy agar plates. The plates were incubated for 24 hours.

Control *Vibrio cholerae* solutions which were not filtered grew 65 colony forming units (cfu) and 71 colony forming units (cfu) at a 1:100 dilution. From this data, the initial titer of the sample was determined. The plates containing the filtrate solutions were analyzed utilizing conventional techniques.

Samples of Zeta Plus® Virosorb® 1MDS media disc were tested for their ability to filter or remove several other bacteria from aqueous solution. The other bacteria are: *E. coli*, *S. typhimurium*, *S. flexineri*, *C. jejuni*, *P. aeruginosa*, and *S. aureus*. Results of testing are reported in Table 2.

The filters provided greater than a 6.0 log reduction in the concentration of *Vibrio cholerae*. The data show that pH appeared to have little impact on *Vibrio cholerae* removal. Significant reductions in the concentration of other bacteria were also observed.

Poliovirus and MS2 Bacteriophage Filtration

Samples of Zeta Plus® Virosorb® 1MDS filter discs were tested for their ability to filter or remove polio virus type 1 or MS2 bacteriophage (typically used as a surrogate for polio virus) from aqueous solution.

Two types of virus solution were used. One solution was a buffer solution containing 0.02 M imidazole and 0.02 M glycine (pH 7.0). The other was dechlorinated tap water. Solution containing MS2 had a concentration of approximately $1x10^6$ MS2/mL. Solution containing polio virus had a concentration of approximately $1x10^5$ polio/mL .

Two layers of 25 mm diameter Zeta Plus® Virosorb® 1MDS filter discs were placed in stainless steel filter housings. Approximately 40 mL of the polio solution or the MS2 solution was forced through th filter utilizing a syringe at a flow rate of approximately 1 to about 3 mL/ sec.

Approximately 0.3 mL of the filtrate was placed in a test-tube with 3 mL glycine/imidazole buffer (pH 7). Further 1:10 dilutions were done to produce a practical plate count.

MS2 plate count measurements were obtained by mixing 0.1 mL of the MS2 solution with 0.3 mL *E. coli* and plating in plate count agar containing crystal violet. Plaques formed by the virus in the bacteria lawn were counted. Polio plate counts measurements were obtained by plating on Green Monkey Kidney cell cultures and observing plaque formation. Results of testing are reported in Tables 3 and 4. The data reported under the headings "Unfiltered" and "Filter Effluent" are expressed in units of microorganisms per mL.

Removal of polio virus appeared to generally increase with increasing pH value. A similar effect was not readily apparent with MS2 bacteriophage. As noted above, pH appeared to have little impact on *Vibrio cholerae* removal

Simian rotavirus Filtration

Samples of Zeta Plus® Virosorb® 1MDS media disc were tested for their ability to filter or remove Simian rotavirus from aqueous solution essentially in accordance with the procedure described above.

Simian rotavirus was added to buffer solution containing 0.02 M imidazole and 0.02 M glycine (pH 7.0). Approximately 50 mL of the seeded solution was passed at a rate of about 1 mL/second through 25 mm filter holders containing two layers of the filter media disc . A second 50 mL portion of the seeded solution was passed through diatomaceous earth coated with aluminum hydroxide and ferric hydroxide on a fiberglass filter.

Dilutions of the initial sample and the effluents from the filters were plated on MA-104 cells. The cells were examined for the presence of cytopathic effects (CPE) for up to six days. Results of testing are reported in Table 5.

While the present invention has been described in connection with certain preferred embodiments, it is to be understood that the subject matter encompassed by way of the present invention is not to be limited to those specific embodiments. On the contrary, it is intended for the subject matter of the invention to include all alternatives, modifications and equivalents as can be included within the spirit and scope of the following claims.

TABLE 1
Results of Coulter Porometer Tests

Sample	Minimum Size(μm)	Maximum Size (μm)	Mean Flow Pore size (μm)
Millipore 0.5 mm Filter	0.30	0.82	0.48
Zeta Plus ® VIROSORB® 1MDS	1.81	9.66.	2.86
Meltblown Polypropylene 1.5 osy (~51 gsm)	8.33	42.75	13.38

TABLE 2
Vibrio cholerae Filtration

Micro-organism	Experimental Conditions	Initial CFU/mL	Final CFU/mL	% Reduction	Log Reduction
V. cholerae 01		$1.0 * 10^6$	0	100%	>6.0
		$6.0 * 10^4$	0	100%	>4.8
		$1.5 * 10^5$	0	100%	>5.2
"		$4.5 * 10^6$	$1.5 * 10^2$	99.997%	4.5
"		$4.25 * 10^6$	$1.5 * 10^4$	99.6%	2.4
"		$1.3 * 10^7$	$2.5 * 10^3$	99.98%	3.7
"		$1.15 * 10^6$	$1.49 * 10^3$	99.87%	2.8
"		$1.1 * 10^5$	0.5	99.9995%	5.35
"		$1.3 * 10^7$	$1.58 * 10^6$	87.8%	0.9
"	0.1% NaCl, pH=4.8 (HCl)	$2.5 * 10^4$	0	100%	>4.3
"	0.1% NaCl pH=7.0 (HCl)	$2.31 * 10^4$	2	99.99%	4.1
"	0.1% PBS pH=7.0	$4.6 * 10^5$	$1.41 * 10^5$	69.3%	0.5
"	0.1% PBS pH=7.0	$7.95 * 10^5$	$8.4 * 10^3$	98.9%	1.98
"	0.1% PBS pH=8.0	$7.45 * 10^5$	$2.81 * 10^4$	96.2%	1.4
"	Lake water*	$4.15 * 10^6$	$1.74 * 10^3$	99.6%	2.4
"		$1.13 * 10^5$	0.5	99.9995%	5.3

TABLE 2 (continued)
Vibrio cholerae Filtration

Micro-organism	Experimental Conditions	Initial CFU/mL	Final CFU/mL	% Reduction	Log Reduction
E. coli		$4.3 * 10^5$	$2.5 * 10^3$	99.4%	2.2
S. typhimurium		$6.85 * 10^5$	0.7	100%	5.7
Shigella flexineri		$5.0 * 10^5$	5	99.999%	5.0
C. jejuni		$4.8 * 10^5$	0	100%	>5.7
V. cholerae 0139	sterile tap H_2O, 0.1% NaCl	$2.63 * 10^5$	$3.87 * 10^2$	99.85%	2.8
P. aeruginosa		$3.85 * 10^5$	0	100%	>5.6
S. aureus		$1.15 * 10^5$	0	100%	>5.1

Table 3

Poliovirus Filtration

Sample	Unfiltered	Filter Effluent	% Reduction	Log. Reduction
Buffer pH 7	3.7×10^5	3.0×10^5	19	- 0.09
Buffer pH 7 (4 layers)	4.2×10^5	2.4×10^5	43	- 0.24
Buffer pH 6	6.4×10^5	3.2×10^5	50	- 0.30
Buffer pH 4	6.4×10^5	6.0×10^4	91	- 1.03
Dechlorinated tap water, pH 6.5	5.4×10^5	4.0×10^5	26	- 0.13
Dechlorinated tap water, pH 4.5	6.4×10^5	1.6×10^5	75	- 0.60

Table 4

MS2 bacteriophage Filtration

Sample	Unfiltered	Filter Effluent	% Reduction	Log. Reduction
Buffer pH 7	1.6×10^5	$<5 \times 10^2$	>99.7	> -2.51
Buffer pH 7 (4 layers)	1.3×10^5	$<5 \times 10^2$	>99.6	> -2.41
Buffer pH 6	2.6×10^4	$<5 \times 10^2$	>98.10	> -1.72
Buffer pH 4	$<5 \times 10^2$	$<5 \times 10^2$	-	-
Dechlorinated tap water, pH 6.5	1.5×10^4	$<5 \times 10^2$	>96.7	> -1.48
Dechlorinated tap water, pH 4.5	1.0×10^4	$<5 \times 10^2$	>95.0	> -1.30

Table 5

Rotovirus Filtration

Sample	Cytopathic effects (+ or -) Undiluted	1/10	1/100	1/1000
Initial	+	+	+	+
Effluent from:				
Virosorb®	+	+	+	+
Modified diato-maceous earth	-	-	-	-

WHAT IS CLAIMED IS:

1. A method of removing a substantial portion of waterborne pathogens from an aqueous liquid contaminated with such waterborne pathogens, the method comprises passing the contaminated aqueous liquid through a chemically charge-modified filter comprising:

a filter sheet having a plurality of individual exposed cellulose fibers and silica based filter materials selected from silica particulates and siliceous fibers;

cationic chemical charge modifiers coated on surfaces of the filter sheet, the chemical charge modifiers comprising:

a primary charge modifier comprising a water soluble organic polymer capable of being adsorbed onto the filter sheet and having a molecular weight of greater than about 1000, each monomer of the polymer having at least one epoxide group capable of bonding on to the individual exposed surfaces of the filter sheet and also having at least one quaternary ammonium group; and

a secondary charge modifier bonded to a portion of the epoxy groups on the organic polymer, wherein the secondary charge modifying agent is an aliphatic polyamine having at least one primary amine or at least two secondary amines;

so that when the contaminated aqueous liquid is passed through the chemically charge-modified filter, a substantial portion of the waterborne pathogens greater than about 0.1 micron in size are adsorbed onto the chemically charge-modified filter.

2. The method of claim 1, wherein the primary charge modifier is polyamine epichlorohydrin and the secondary charge modifier is tetraethylene pentamine.

3. The method of claim 1, wherein the waterborne pathogens are greater than about 0.1 micron in size.

4. The method of claim 1, wherein the waterborne pathogens are selected from *Vibrio cholerae*, *E. coli*, *S typhimurium*, *S. flexineri*, *C. jejuni*, *P. aeruginosa*, and *S. aureus*.

5. The method of claim 4, wherein the reduction of *Vibrio cholerae* is greater than a log 2 reduction.

6. The method of claim 4, wherein the reduction of *Vibrio cholerae* is greater than a log 5 reduction.

7. The method of claim 1, wherein the aqueous liquid is passed through th filter sheet having a three-dimensional form.

8. The method of claim 7, wherein the three-dimensional form is cylindrical.

9. The method of claim 1, wherein the aqueous liquid has a pH ranging from about 5 to about 9.

10. A method of removing a substantial portion of of *Vibrio cholerae* from water contaminated with such waterborne pathogens to produce potable water, the method comprises passing the contaminated water through a chemically charge-modified filter comprising:

a filter sheet having a plurality of individual exposed cellulose fibers and silica based filter materials selected from silica particulates and siliceous fibers;

cationic chemical charge modifiers coated on surfaces of the filter sheet, the chemical charge modifiers comprising:

a primary charge modifier comprising a water soluble organic polymer capable of being adsorbed onto the filter sheet and having a molecular weight of greater than about 1000, each monomer of the polymer having at least one epoxide group capable of bonding on to the individual exposed surfaces of the filter sheet and also having at least one quaternary ammonium group; and

a secondary charge modifier bonded to a portion of the epoxy groups on the organic polymer, wherein the secondary charge modifying agent is an aliphatic polyamine having at least one primary amine or at least two secondary amines;

so that when the contaminated water is passed through the chemically charge-modified filter, a substantial portion of the of *Vibrio cholerae* is adsorbed onto the chemically charge-modified filter to yield potable water.

11. The method of claim 10, wherein the primary charge modifier is polyamine epichlorohydrin and the secondary charge modifier is tetraethylene pentamine.

12. The method of claim 10, wherein the reduction of *Vibrio cholerae* is greater than a log 2 reduction.

13. The method of claim 12, wherein the reduction of *Vibrio cholerae* is greater than a log 5 reduction.

14. The method of claim 10, wherein the aqueous liquid is passed through the filter sheet having a three-dimensional form.

15. The method of claim 14, wherein the three-dimensional form is cylindrical.

16. The method of claim 10, wherein the aqueous liquid has a pH ranging from about 5 to about 9.

17. A method of removing a substantial portion of of *Vibrio cholerae* from an aqueous liquid contaminated with such waterborne pathogens, the method comprises passing the contaminated aqueous liquid through a chemically charge-modified filter comprising:

a filter sheet having a plurality of individual exposed cellulose fibers and silica based filter materials selected from silica particulates and siliceous fibers;

cationic chemical charge modifiers coated on surfaces of the filter sheet, the chemical charge modifiers comprising:

a primary charge modifier comprising a water soluble organic polymer capable of being adsorbed onto the filter sheet and having a molecular weight of greater than about 1000, each monomer of the polymer having at least one epoxide group capable of bonding to the individual exposed surfaces of the filter sheet and also having at least one quaternary ammonium group; and

a secondary charge modifier bonded to a portion of the epoxy groups on the organic polymer, wherein the secondary charge modifying agent is an aliphatic polyamine having at least one primary amine or at least two secondary amines; a filter sheet having a plurality of individual exposed surfaces; and

so that when the contaminated aqueous liquid is passed through the chemically charge-modified filter, a substantial portion of the of *Vibrio cholerae* are adsorbed onto the chemically charge-modified filter.

18. The method of claim 17, wherein the reduction of *Vibrio cholerae* is greater than a log 2 reduction.

19. The method of claim 18, wherein the reduction of *Vibrio cholerae* is greater than a log 5 reduction.

20. The method of claim 17, wherein the aqueous liquid is passed through the filter sheet having a three-dimensional form.

FIG. 1

INTERNATIONAL SEARCH REPORT

Intern. ial Application No
PCT/US 97/10722

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01D39/18 B01D39/14 A61L2/00 A61L2/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01D A61L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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Intern nal Application No
PCT/US 97/10722

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